-- FLUORINE AND ITS COMPOUNDS --

(Fluorine) (Hydrofluoric Acid) (Sodium Fluoride)
(Silicon Fluoride) (Cryolite)
(Ammonium Bifluoride)

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-- FLUORINE AND ITS COMPOUNDS --

Lavoisier (1743-1794) recognized the distinctive chemical character of fluorides and Davy (1778-1829) established the elementary character of fluorine. However, the isolation of fluorine was not accomplished until 1887 when Moissan using low temperature electrolysis isolated this active gas. He prepared vessels from transparent fluorspar (calcium fluoride) to observe some of its physical properties.

Reports of poisonings by fluorides were not common before 1900. It is stated that a Belgian chemist died from the effects of hydrofluoric acid fumes in an attempt to isolate the element fluorine. Cameron in 1887 described two fatal cases of fluorine poisoning among superphosphate workers. In 1900 respiratory troubles due to fluorides were reported in certain German factories.

The deaths of 60 inhabitants of the Meuse valley in Belgium during the fog disaster in December 1930, have been attributed to fluorine intoxication. It was revealed that within a short distance in this valley 15 factories were using fluorine compounds in a way that gaseous fluorine substances might be emitted into the atmosphere. The presence of these gases combined with unusual climatic and topographic conditions made this disaster possible.

In 1931 Smith, Lantz, and Smith showed the relation between the fluoride content of water supplies and the mottling of tooth enamel. This discovery has greatly extended the relation of fluorides to public health problems.

GENERAL INFORMATION

CHEMICAL FORMULA AND SYNONYMS:

(Fluorine) F_2.

(Hydrofluoric acid) H_2F_2, fluorhydric acid, hydrogen fluoride.

(Sodium fluoride) NaF, fluorol.

(Silicon fluoride) SiF_4, silicontetrafluoride.

(Cryolite) Na_3AlF_6, cryolith, greenland spar, ice stone, kryolith.

(Ammonium bifluoride) NH_4HF_2.

PROPERTIES:

(Fluorine) Colorless gas; corrosive; poisonous! Sp. gr. (liquid) 1.11, (gas) 1.31(A); m.p. -223°C.; b.p. -187°C. Decomposes in water.

(Hydrofluoric acid) Clear, colorless, fuming, mobile, corrosive liquid.

Produces terrible sores when allowed to touch the skin. Sp. gr. 0.988; m.p. (anhydrous liquid) -83°C.; b.p. (anhydrous liquid) 19.44°C. Soluble in water. Wt. per liter of gas, 0.83 gr.

(Sodium fluoride) Clear, lustrous crystals or white powder; poisonous! Sp. gr. 2.79; m.p. 992°C. Soluble in water; slightly soluble in alcohol.

(Silicon fluoride) Colorless gas; suffocating odor; fumes strongly in air. Absorbed readily in large quantities by water with partial decomposition. Sp. gr. 3.57 (A), m.p. -77°C, b.p. -65°C. at 1810mm.

(Cryolite) A natural fluoride of sodium and aluminum. Usually colorless to snow white, but sometimes reddish or brownish or even black. Vitreous, greasy, moist-looking or pearly luster. Sp. gr. 2.9 to 3; hardness 2.5.

(Ammonium bifluoride) White crystals. Sp. gr. 1.211. Soluble in cold water; decomposes in hot water.

OCCURRENCE:

(Cryolite) Greenland, Russia, and United States (Colorado).

PREPARATION:

(Fluorine) (a) By electrical decomposition of anhydrous hydrofluoric acid at -23°C. or (b) electrolysis of fused potassium hydrogen fluoride.

(Hydrofluoric acid) Powdered calcium fluoride is treated with sulfuric acid and the mixture distilled in a platinum retort. The hydrofluoric acid gas passes over and is dissolved in distilled water.

(Sodium fluoride) By adding sodium carbonate to hydrofluoric acid.

(Silicon fluoride) (1) Action of hydrofluoric acid or concentrated sulfuric acid and a metallic fluoride on silica or silicates. (2) Direct synthesis.

(Ammonium bifluoride) Action of ammonium hydroxide on hydrofluoric acid with subsequent crystallization.

USES:

(Fluorine) Organic synthesis; fluorine compounds.

(Hydrofluoric acid) Chemicals (fluorides, electrolytic manufacture of chlorates and persulfates, hydrogen peroxide from peroxide of sodium); analytical reagent; ceramics (to increase porosity); breweries and distilleries (antiseptic, retarding injurious fermentation); frosted glassware; etching glass; reagent in manufacture of filter paper; purification of beet sugar; yeast manufacture; manufacture of chemical and physical apparatus, for etching divisions on thermometer stems,

etc., cleaning copper and brass; removal of sand particles in metallic castings; graphite purification.

(Sodium fluoride) Antiseptic and antifermentative in alcohol distilleries, etc.; food preservative; roach and rat poison; medicine; flux; enamels.

(Silicon fluoride) Manufacture of fluosilicic acid; chemical analysis; nuisance by-product in fertilizer manufacture.

(Cryolite) Chemicals (sodium salts); aluminum manufacture (flux); glass (opacity); manufacture of vitreous enamels.

(Ammonium bifluoride) Ceramics; chemical reagent; etching glass (White acid); sterilizer for brewery, dairy, and other equipment.

INDUSTRIAL HEALTH ASPECTS

MODES OF ENTRANCE:

(Fluorine) Inhalation.

(Hydrofluoric acid) Inhalation or ingestion.

(Sodium fluoride) Inhalation or ingestion.

(Silicon fluoride) Inhalation.

(Cryolite) Inhalation or ingestion.

(Ammonium bifluoride) Inhalation or ingestion.

SYMPTOMS OF INDUSTRIAL POISONING:

(Fluorine) This gas in the elementary state is rare and has little industrial significance. It is extremely active and even more corrosive than hydrofluoric acid. In the presence of moisture, fluorine gas is quickly converted into hydrofluoric acid and ozone (see hydrofluoric acid).

(Hydrofluoric acid) It is intensely irritating and caustic and when inhaled may result in coryza, bronchial catarrh with spasmodic coughing, a sense of constricted breathing and pulmonary edema. It causes irritation and ulceration of mucous membranes; also may cause lachrymation and salivation. The damage is generally limited to severe dermatitis, often with vesicles and necrotic ulcers which become indurated and difficult to heal. May cause painful ulcers of the cuticle, erosion and formation of vesicles, suppuration under the fingernails.

(Sodium fluoride) Chronic poisoning causes symptoms like alkaline compounds; if ingested is extremely caustic. It is a general protoplasmic poison and has a strong local irritant action. Absorption of small amounts (fractions of a gram) of the salts can result in symptoms of nausea and vomiting, gastric pain, salivation, pruritis and diarrhea. Larger amounts (over one gram) of the salts may cause vomiting, cramps, fibrilliary tremors, rigidity followed by muscular paralysis, acceleration followed by paralysis or respiration and paralysis of the central nervous system. Ingestion of larger amounts of salts give rise to acute poisoning with rapid fatal termination.

(Cryolite) Chronic fluorosis from the inhalation of this dust has been reported in Europe with mottling and degenerative changes in the teeth and osteosclerosis with ligament calcification. There is also loss of weight, dyspnea on exertion, loss of appetite and vomiting, with some anemia. These may disappear when exposure ceases.

(Ammonium bifluoride) Chronic poisoning may produce symptoms of vomiting, cramps, tremors, muscular spasticity, difficult respirations, and decrease of blood calcium.

INDUSTRIES AND OCCUPATIONS

INDUSTRIES: Ohio Industries using fluorine and its compounds as indicated in the Ohio Industrial Hygiene Survey are listed as follows:

- Brass factories
- Chemicals
- Distilled malts and wines
- Dry cleaning and dyeing
- Electric fixtures
- Electrical machinery
- Electro-plating
- Fertilizer factories
- Foundries
- Glass factories
- Jewelry
- Laundries
- Metal furniture
- Other manufacturing plants
- Printing
- Soap factories
- Storage batteries
- Tin and enameled ware

OCCUPATIONS: Occupations in Ohio where contact with fluorine and its compounds was indicated are listed as follows:

- Autoclave men (chemicals)
- Beaders (tin and enameled ware)
- Blowers (glass factory)
- Brew masters (distilled malts and wines)
- Burners (tin and enameled ware)
- Car men (fertilizer factories)
- Chemists (distilled malts and wines)
- Den men (fertilizer factories)
- Dippers (tin and enameled ware)
- Elevator men (fertilizer factories)
- Enamel makers (tin and enameled ware)
- Etchers (other manufacturing plants; electrical machinery)
- Evaporator men (chemicals)
- Fermenting cellar workers (distilled malts and wines)
- Foremen (distilled malts and wines; jewelry)
- Frosters (electric fixtures)
- Furniture cleaners (dry cleaning and dyeing)
- Hot galvanizers (electrical machinery)
- Insecticide mixers (soap factories)
- Kettle men (distilled malts and wines)
- Laborers (electric fixtures; tin and enameled ware; foundries; glass factories)
- Machinist (storage batteries)
- Mill men (distilled malts and wines)
- Mixers (tin and enameled ware; fertilizer factories; glass factories)
- Pit cutters (fertilizer factories)
- Platers (electrical machinery; metal furniture; printing; brass factories; storage batteries)
- Pressers (glass factories)
- Processors (electrical machinery)
- Rimmers (tin and enameled ware)
- Rug cleaners (dry cleaning and dyeing)
- Smelters (tin and enameled ware)
- Spongers (tin and enameled ware)
- Spotters (dry cleaning and dyeing)
- Sprayers (tin and enameled ware)
- Storage men (distilled malts and wines)
- Tinners (electro-plating)
- Wash house men (distilled malts and wines)
- Washing machine operators (laundries)
- Weigh car operators (tin and enameled ware)

Occupations which offer contact with fluorine and its compounds but not listed in the Ohio Survey are:*

Aluminum extractors	Fertilizer makers
Antimony-fluoride extractors	Gold refiners
Art glass workers	Hydrofluoric-acid makers
Bleachers	Phosphorus extractors
Dyers	Silicate extractors

*Dublin, L.I., and Vane, R.J.: Occupation Hazards and Diagnostic Signs. U.S. Department of Labor, Bureau of Labor Statistics, Bulletin 582:38, 1933.

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COMPARATIVE TOXICITY OF FLUORINE COMPOUNDS.

M.C. Smith, and R.M. Leverton. Indust. and Engin. Chem., July 1934, vol. 26, pp. 791-797.

Abstracted in J. of Ind. Hygiene, vol. 16, no. 5, p. 97 (abstract section) Sept. 1934.

The use of drinking water containing fluorine in concentrations of one part per million or more is recognized as the cause of mottled enamel, a defect of human teeth. The increasing use of fluorine compounds as spray insecticides has prompted this study of the comparative toxicity of different compounds of fluorine. The following compounds of fluorine are used: sodium, potassium, ammonium, and calcium fluorides; sodium, potassium and barium fluosilicates; and natural cryolite (sodium aluminum fluoride). A comparison is made of their effect upon growth rate, food consumption, efficiency of utilization of food, reproduction, mortality, and teeth, when supplied to young albino rats at the same fluorine concentration. Wide differences in toxicity among these compounds are found when the effect upon growth, food utilization, and damage to the teeth are considered, which may or not be a reflection of difference in their solubility. From the standpoint of initial damage to the teeth, however, all these compounds of fluorine are found to be equally toxic. Fourteen parts per million of fluorine (from any source) in the diet of the rats leaves a mark upon the rat incisors. The significance of these findings in relation to the spray residue problem and human mottled enamel is discussed.--Author's summary.

ACUTE FLUORINE POISONING.

K. Roholm. Deutsch. Ztschr. f. d. ges. gerichtl. Med., vol. 27, pp. 174-188 (1936).

Abstracted in J. of Ind. Hygiene, vol. 19, no. 2, p. 38 (abstract section) Feb. 1937.

The author reviews acute fluorine poisoning of which 112 cases have been reported with 60 deaths. Most of them were suicides or people who took the poison by mistake. The picture shows acute irritation of the stomach and intestines (vomiting, diarrhea) and tetany-like cramps and paralysis. In superphosphate, aluminum, gas, enamel and chemical factories, gaseous fluorine compounds are produced and industrial poisoning thus made possible. Also in the great fog catastrophe in Belgium in 1930 fluorine compounds must have played a part.--L. Teleky.

FLUOROSIS AND FLUORIC CACHEXIA.

Foreign Letter (Italy), Jour. Am. Med. Assn., July 28, 1928, vol. 91, p. 260.

Abstracted in J. of Ind. Hygiene, vol. 11, no. 3, pp. 55-56 (abstract section) Mar. 1929.

Before The Associazione Medica of Trieste, Professor Cristiani presented recently a communication on fluorosis. The author pointed out that chronic intoxication with fluorine is a new disease, for it is only a few years

since the soluble salts of fluorine first began to be used as a food preservative, and still more recently that fluorine began to be employed more widely in the industries. In Switzerland, in the environs of an aluminum factory, from which large quantities of fluorine vapors were thrown off, there developed a disease among the cattle, from which 150 died. As the owners of the factory refused to admit that their plant had anything to do with the death of the cattle, Professor Cristiani was engaged to study the problem. He demonstrated that, whereas a normal guinea-pig lives from five to six years, those fed with forage treated with fluorine vapors die in from three to six months from chronic intoxication and fluoric cacheria. Fluorine is at present employed in several countries for the manufacture of insect powders and for the conservation of butter, wines, syrups, and milk. The use of fluorine in milk is especially dangerous, since the feeding of milk inpregnated with fluorine causes in children a fluorosis that is fatal.--K.R.D.

FLUORINE INTOXICATION IN CRYOLITE WORKERS.

K. Roholm. Hospitalstidende, vol. 79, pp. 981-1002 (Sept. 29, 1936).
Abstracted in J. of Ind. Hygiene, vol. 19, no. 3, p. 60 (abstract section) Mar. 1937.

Roholm says that chronic resorptive fluorine intoxication differs clinically, roentgenologically and anatomopathologically from the known sclerosing diseases of the bones. Intoxication from fluorine results from inhalation of a daily dose of from about 0.2-0.35 mgm. of fluorine/kgm. of body weight. Examination of 68 workers on cryolite exposed to the dust showed that the majority were affected. The acute symptoms are loss of weight, nausea and vomiting; the chronic symptoms, functional dyspnea, pain of rheumatic character, stiffness and constipation. The workers soon become inured to the effects. In fifty-seven (85.8%) of the workers there was sclerosis of the bones of the body, as described by Moller and Gudjonsson, especially of the spinal column, pelvis and ribs. In some cases the mobility in the spinal column and thorax was reduced. The general condition was not disturbed. Postmortem in two workers who died from intercurrent diseases revealed no organic changes definitely attributable to the intoxication. The bones weighed up to 3 times the normal and were chalky white, with extensive periosteal deposits and calcification of ligaments. The bony system contained an average of about 60 times the normal amount of fluorine. The fluorine content was increased in the lungs. Evidence indicates that when the intake of fluorine ceases the sclerotic bony tissue is replaced by normal tissue; the ligament calcifications seem to disappear incompletely. As fluorine is eliminated in the milk, mottled teeth in the children of women workers may result if lactation is contained long.--J.A.M.A.

CHRONIC FLUORINE POISONING, SEEN FROM THE ROENTGENOLOGICAL STANDPOINT.

P.F. Moller. Brit. J. Radiol., vol. 12, pp. 13-20 (Jan. 1939).
Abstracted in J. of Ind. Hygiene, vol. 21, no. 6, pp. 136-137 (abstract section) June 1939.

This subject was first called to the attention of radiologists by P. Flemming Moller. Doctor Moller in his address before the Fourth Annual Meeting of the British Association of Radiologists states that the condition was recognized as far back as 1889 by Brandl and Tappeiner who demonstrated

chronic fluorine poisoning in a dog. Chronic fluorine poisoning in man was not known until 1931 when in the course of some investigations in silicosis in factory workers, the author discovered curious changes in the bones of a number of workers engaged in a cryolite factory.

The symptoms of the affected individuals corresponded both clinically and pathologically with those which had been found in animal experimentation. These symptoms included lack of appetite, nausea, and vomiting. They were acute in character and disappeared when the individuals went into the open air. Apparently the workers after a while developed a tolerance for the dust. Cryolite is a fluoride of sodium and aluminum and contains about 54% of fluorine. The symptoms depend upon working in a dust laden atmosphere. Some of the patients complain of chronic constipation. Others had chest symptoms which were largely those of dyspnea on exertion, cough, and expectoration. A few complained of rheumatic pains in the body and extremities, or generalized body stiffness.

The principal sign of fluorine poisoning was the changes occurring in the bones, especially the spongy bones. In the affected individuals, there was almost complete disappearance of normal bony structure, the bones of the vertebrae and spine having almost a milky white opacity. In the severe cases, extensive calcification occurred in the ligaments and fibrocartilaginous attachments.

In the extremities, the compact layers of bone were much thickened and the marrow cavities narrowed. The small bones of the hands and feet showed a similar appearance. The degree of sclerosis depends on the length of time the individual is engaged in dusty work. The earliest changes were noted after 2½ years; more extensive changes occurred after 4 to 11 years. The mobility of the spine was restricted and the amount of restriction depended upon the degree of the disease.

Doctor Roholm has carried on extensive chemical investigations. His work indicates that chronic fluorine poisoning may occur from a number of industries in which fluorine, which occurs so extensively in nature, is used. Fluorine is a constant element of volcanic rock species and is found widely distributed in inanimate nature, in soil, and in fresh and salt water. Calcium fluoride is very widely found in nature. Other minerals, such as cryolite and phosphorite, contain relatively large amounts of fluorine. Doctor Paul Bishop in this country reported a case of fluorine poisoning occurring in a fertilizer worker in 1936. This is the only case that I have seen personally. From what Moller describes in his original article, chronic fluorine poisoning is a definite dust hazard and it is entirely possible with an increased number of examinations of bone that the condition may be found with increasing frequency.

Another feature of the condition concerns the teeth. The changes in the teeth have been recognized by workers in America, Italy, Spain, England, India, and Africa. The changes in the teeth have been described as mottled teeth or "darmous."

It is extremely important that radiologists recognize the incidence of this condition. In adults, the roentgen findings must be differentiated from prostatic carcinoma and syphilis. Both of these conditions may give, on occasions, roentgen appearances that simulate chronic fluorine poisoning. In children, conditions such as the mineral poisonings, including lead, phosphorus, and manganese, and unknown conditions such as marble bones, may have to be considered in differential diagnosis because all of these conditions effect the same bones as in fluorine poisoning. In that this condition may be contracted through drinking water which passes through deposits of phosphorite containing fluorine, individuals not actually exposed to a dusty hazard of fluorine may be affected.

The original article is illustrated with several roentgenograms showing the dense marble-like types of bone, as well as pathological specimens of bones and teeth.--E.P. Pendergrass.

FOG CATASTROPHE IN INDUSTRIAL SECTION SOUTH OF LIEGE.

W.S. van Leeuwen. Abstr. as follows from Munchen. med. Wchnschr., Jan. 9, 1931, vol. 78, p. 49, in Jour. Am. Med. Assn., April 18, 1931, vol. 96, p. 1347.

Abstracted in J. of Ind. Hygiene, vol. 13, no. 7, pp. 159-160 (abstract section) Sept. 1931.

Storm van Leeuwen describes the fog catastrophe in the valley of the Meuse, during which hundreds of persons became ill and sixty-three died. On December 1, a Monday, a fog developed in Belgium and in the Netherlands. In the valley of the Meuse the fog was especially heavy, and on account of an absolute calm it did not lift until Thursday afternoon. On Friday it again became foggy and it remained so until Sunday. On Tuesday and Wednesday the fog was especially heavy. On Wednesday a large number of persons complained of irritations in the nose, mouth, throat, trachea, and bronchi. The mucous membranes were red and swollen. Necropsies later revealed that these inflammations reached down into the large ramifications of the bronchi. The patients coughed and the respiration frequency was more than 40 a minute. In the serious cases dyspnea, dilatation of the heart, high pulse frequency, and cyanosis developed. Signs of pneumonia were not present. Injections of epinephrine brought temporary improvement, and cardiac stimulants were also administered. Among those who were seriously ill, and especially among those who died, there were many old persons, also persons with asthma, bronchitis, and heart disease. However, it was also noted that young persons who had been healthy before became seriously ill and that many others felt an unpleasant irritation in the throat. The sixty-three fatalities all occurred within twenty-four hours and in the narrow valley south of Liege. In discussing the causes of the catastrophe the author points out that the opinion that the heavy, cold fog is irrespirable and that the fatalities were due to suffocation from lack of oxygen is not tenable because heavy, cold fogs are quite frequent on the sea coast of the Netherlands, and yet there are no fatalities. The theories of war gases and of Sahara sands are likewise dismissed. In traveling through this region the author noted numerous factories, such as zinc industries, superphosphate factories, and other industrial plants. It may be assumed that even under normal conditions the air contains irritative substances such as sulphur dioxide and hydrofluoric

acid. It is also known that this region is fit for neither agriculture nor cattle raising. That this is due to the presence of the factories is proved by the fact that the cattle raisers had a lawsuit against the manufacturers and were paid damages. The cold and heavy fog and the absolute calmness during the first days of December prevented ventilation, and it is also possible that some of the factories discharged an abnormally large amount of poisonous substances during these days. This catastrophe teaches that the harmfulness of gases discharged by certain industries should not be estimated on an ordinary day, but that the concentrating effects of fogs should be taken into consideration.--C.K.D.

HYDROFLUORIC ACID FUMES.

C.M. Salls. Indust. Hyg. Bull., Sept. 1924, vol. 1, p. 10.

Abstracted in J. of Ind. Hygiene, vol. 7, no. 1, p. 9 (abstract section) Jan. 1925.

Exposure to hydrofluoric acid fumes produces intense irritation of the eyelids and conjunctiva, coryza, bronchial catarrh, and ulceration of the nostrils, gums, and oral mucous membrane; also painful blisters and ulcers of the cuticle, suppuration under the loss of the finger nails.

This acid is used to produce etchings on fancy glass containers, in the manufacture of pottery, glassware, and fertilizer and for the bleaching of cane for chair seats. To produce etching, glass is dipped in a mixture of hydrofluoric acid and alkali fluoride and other salts. If the solution contains too much hydrofluoric acid the etching is coarse-grained and irregular, and if it contains too little of the acid the etching is transparent. The concentration of the acid, however, has nothing to do with the degree of opacity, for the neutral components enter into the reaction in some manner. Safe and sane mixtures for etching can thus be made by reducing the concentration of hydrofluoric acid and increasing the percentage of neutral components.--B.L.G.

DETERMINATION OF FLOURINE SPRAY RESIDUE ON TOMATOES.

W. Ferdinand Eberz, Frank C. Lamb, and C.E. Lachele. Ind. Eng. Chem., Anal. Ed. 10, 259-262 (1938).

Abstracted in chemical abstracts, vol. 32, 5094.

The F is detd. by a modification of the Willard and Winter method (C.A. 27, 681). A mixt. of $Co(NO_3)_2$ and K_2CrO_4 is used to match the end point color with Nessler tubes. MgO is added in the ashing. The use of a single distn. with perchloric acid gave an av. recovery of 102.4% F.

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